

GENERAL PAPERS - POSTER SESSION
PRESENTED BEFORE THE DIVISION OF PETROLEUM CHEMISTRY, INC.
AMERICAN CHEMICAL SOCIETY
WASHINGTON, D. C. MEETING, AUGUST 28-SEPTEMBER 2, 1983

DEVELOPMENT OF AN ALTERNATIVE S.A.R.A. METHOD FOR THE
CHARACTERIZATION OF COAL-DERIVED LIQUIDS

By

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INTRODUCTION

Coal-derived liquids have been studied extensively, because of their potential applications in many fields such as fuel and feedstocks generation (1). One of the most popular methods by which to characterize fossil fuels is by fractionation of the sample into saturates, aromatics, resins and asphaltenes (S.A.R.A.). Two different approaches are widely used for this purpose: solvent extraction and liquid chromatography. Although much work has been done using these two approaches, characterization of fossil fuels is still unsatisfactory and exhaustive research is still required. Solvent extraction methods currently used, though simple and inexpensive, present problems with reproducibility, time consumption, solvent evaporation, co-extraction and loss of volatiles (2, 3). In most of the liquid chromatographic methods used, the fossil fuel extract is first treated with a non-polar hydrocarbon (such as n-pentane) to precipitate the asphaltenes and the remaining solution is applied to an Attapulgis clay column to separate resins from oils. Finally, the oils are fractionated to saturates and aromatics on alumina and/or silica columns (4). All these steps, in addition to being unnecessary and inconvenient, do not provide the actual group-type distribution in the extract since part of the resins could be co-precipitated with asphaltenes (5). With these problems in mind, we have developed and applied an alternative S.A.R.A. method for the characterization of Brazilian coal-derived liquids.

RESULTS AND DISCUSSION

Fractionation by Solvent Extraction

Coal was finely ground, sieved through a 60 mesh (U. S. Standard) sieve, extracted with different solvents for 30 minutes using a magnetic stirrer (100 ml of solvent to 10 g of coal). Results showed that stirring time is not critical. After one hour of stirring with hexane, the unextracted coal was 96.6% of the original sample, while after 12 hours it was 95.6%. Following extraction, the solvent was evaporated and the extract redissolved in 2 ml of solvent. Asphaltenes were precipitated by adding 80 ml of n-pentane to the concentrated extract solution (volume ratio of 40 to 1). In all experiments solvents were evaporated by a combination of rotary evaporation for sample concentration and controlled heating under nitrogen flow until dryness of the extract. Figure 1 shows the results of a study comparing the relative amounts of asphaltenes and maltenes present in the "Mina do Leao" (high-ash Brazilian coal). The relative amounts extracted by the different solvents are displayed in Figure 2. Although pyridine is the best solvent examined, we decided to use tetrahydrofuran (THF) since it has a similar performance and it is less toxic and less polar.

In a different set of experiments, the fractionation of the THF coal extract into asphaltols, asphaltenes and oils was carried out utilizing the schematic shown in Figure 3. The results of this study appear in Table I.

Fractionation by Column Chromatography

A 50 cm (L) x 11 mm (I.D.) glass column fitted with a teflon stopcock was dry or slurry packed for comparison purposes. Dry packing was done by constantly tapping the column while adding 2 g of the packing material in small portions. A plug of glass wool and a layer of white sand (ca. 0.5 cm) on the top were used to support the solid adsorbent and to prevent it from washing through the stopcock. Slurry packing was performed by first adding the solid adsorbent a little at a time to hexane in a beaker, swirling the beaker and pouring the slurry into a draining column (previously filled about 1/3 full with the first eluent, hexane). The results of a comparative study using different packing techniques and materials are displayed in Table II. A set of five identical columns was employed, to determine the reproducibility of each system as applied to a hexane coal extract. For this study, the hexane soluble materials were filtered following extraction into a 100 ml

volumetric flask. 10 ml of this stock solution was loaded into the chromatographic column. The eluents used to generate the fractions were hexane (50 ml), toluene (75 ml) and methanol (50 ml) for saturates, aromatics and resins, respectively, following precipitation of asphaltenes, in accordance with the Phillips method (6). The results show that slurry packing with silica is the most reproducible system investigated. (It is well-established in the literature that asphaltols are highly adsorbed on alumina, while fewer substances are adsorbed on silica gel because of its mildly acidic properties (7, 8).)

TABLE I
SOLUBILITY CHARACTERISTICS OF HIGH-ASH BRAZILIAN COAL THF EXTRACT

Sample	Wt % Asphaltols	Wt % Asphaltenes	Wt % Oils
1	38.5	35.2	26.3
2	38.5	32.4	29.1
3	37.8	36.9	25.4
4	36.4	37.6	26.0
5	42.1	34.8	23.1
	\bar{x}	38.7	35.4
	σ	2.1	2.0
	R. S. D.	5.4	5.7
			8.3

TABLE II
COMPARISON OF DIFFERENT PACKING SYSTEMS AS APPLIED TO HEXANE COAL EXTRACT

Group Type	Column Type ^a :	1	2	3
Saturates	Wt %	40.4	35.3	24.3
	σ	8.8	3.4	2.3
	R. S. D.	22	9.8	9.5
Aromatics	Wt %	30.1	22.4	30.1
	σ	5.9	3.1	2.2
	R. S. D.	20	14	7.1
Resins	Wt %	29.4	42.3	45.6
	σ	10	2.5	1.8
	R. S. D.	35	5.8	4.0

a. 1=dry-packed alumina; 2=slurry-packed alumina;
3=slurry-packed silica.

Since the best performance was shown with THF as extracting agent and silica gel as an adsorbent for slurry packing technique, we have applied the whole coal extract (a maximum of 200 mg) to the column to avoid problems associated with the asphaltenes precipitating in non-polar solvents. The characteristics of the chromatographic elution utilizing this new system as well as the relative group type distribution of the THF coal extract appear in Table III.

TABLE III
CHROMATOGRAPHIC ELUTION CHARACTERISTICS AND RELATIVE GROUP TYPE DISTRIBUTION OF THF COAL EXTRACT

Eluent	Volume of Eluent	Color of Eluent	Identity	Wt %
Hexane	50 ml	Colorless	Saturates	3.3
Toluene	75 ml	Orange	Aromatics	20.2
Methanol	50 ml	Red-Wine	Resins	51.8
THF	50 ml	Dark Brown	Asphaltenes	24.7

100.0

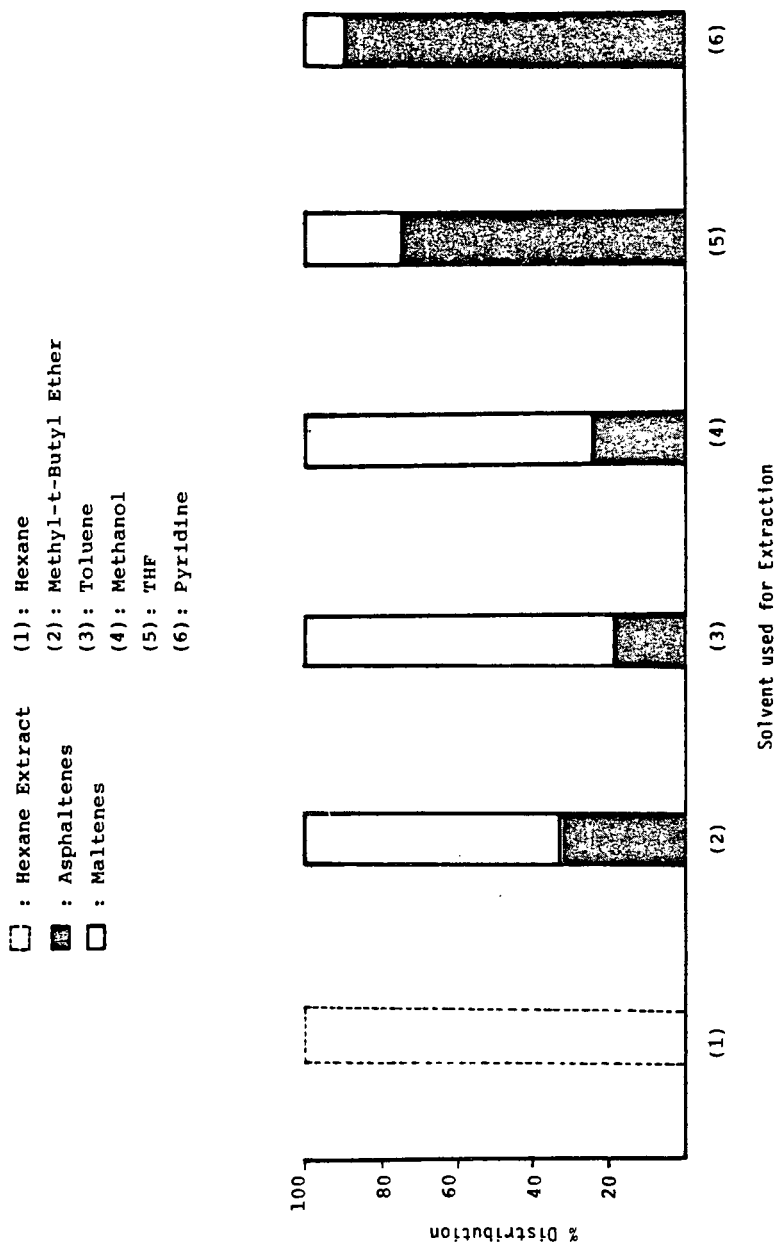


Figure 1. Relative amounts of asphaltenes and maltenes in the high-ash Brazilian coal.

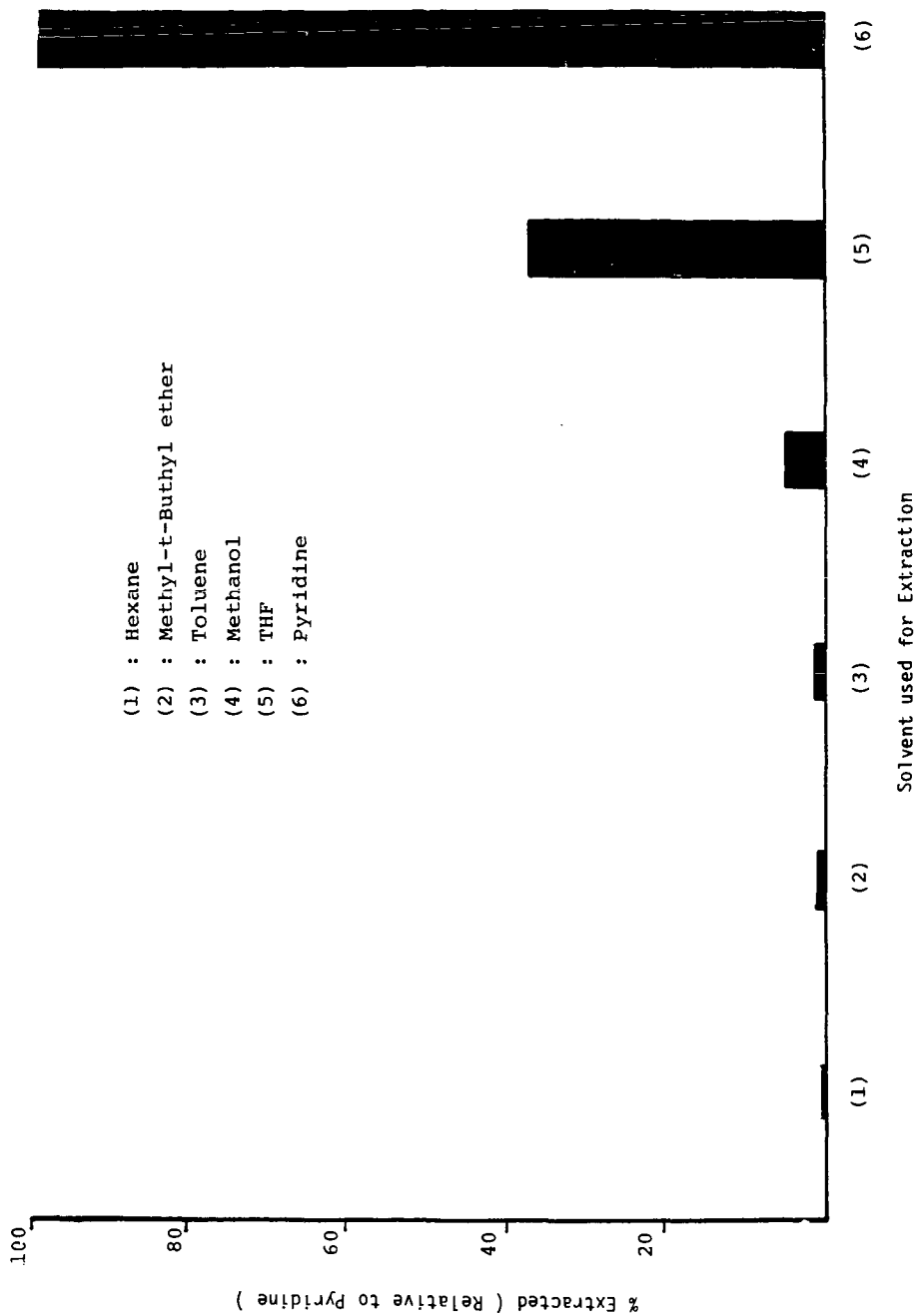
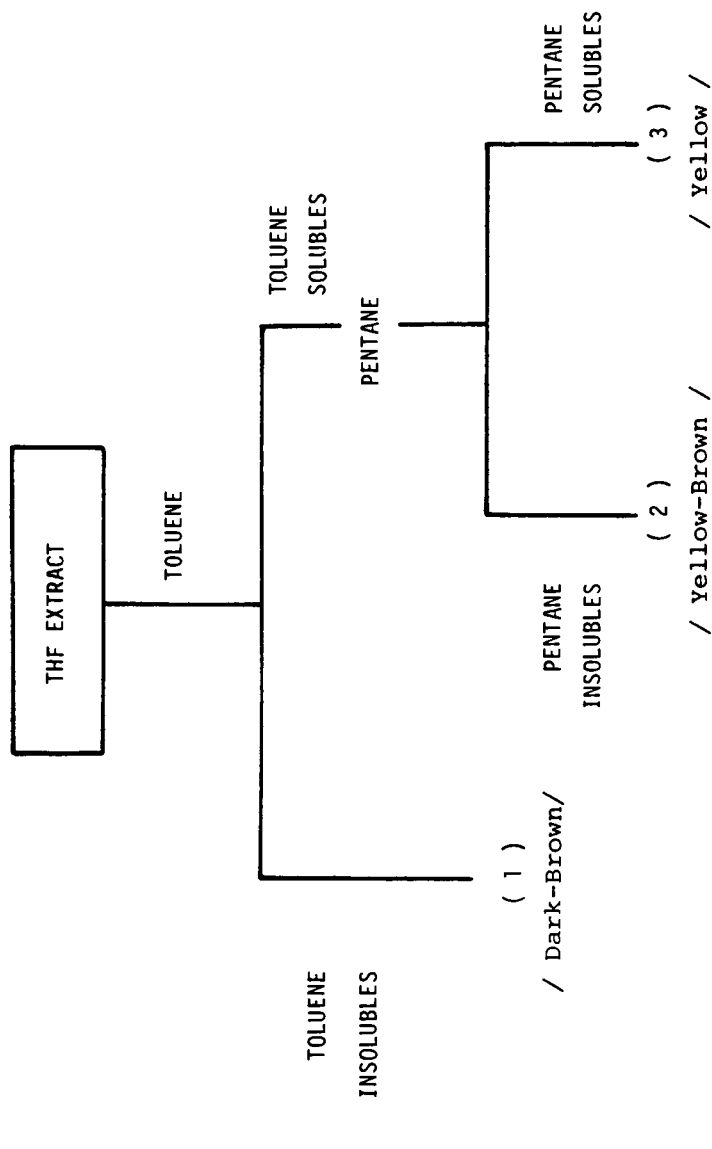


Figure 2. Percentage extracted (relative to Pyridine) using different solvents.



- (1): Asphaltols
 (2): Asphaltenes
 (3): Oils

Figure 3. Fractionation schematic of the THF extract

CONCLUSION

Compared with methods of characterization of coal extract described in the literature, the method we have developed has the following advantages:

1. Extraction Step: Using THF instead of hexane, pyridine, toluene, etc., gives more reproducible results and avoids extracting very polar compounds and loss of volatiles during the evaporation step. Magnetic stirring instead of manual stirring or Soxhlet extraction is an easier, faster and more reproducible extraction procedure.

2. Column Chromatography: Slurry packing with silica permits a better stationary bed and, at the same time, avoids irreversible adsorption. By fractionating the whole THF coal extract, one avoids the precipitation of asphaltenes prior to column chromatography. In addition, fractionating the whole extract permits collection of the four S.A.R.A. (saturates, aromatics, resins and asphaltenes) fractions for further characterization.

ACKNOWLEDGMENTS

F. M. Lancas would like to thank Fundacao de Amparo a Pesquisa do Estado de Sao Paulo (FAPESP) for the fellowship (Processo 16-Quimica 81/0557-2) and Universidade de Sao Paulo for the free absence.

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